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April 13, 2015

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Rome, Italy
May 18, 2015 through May 21, 2015

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Synthesis and Small-scale Performance Characterization of New Insensitive Energetic Compounds

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Abstract:

Insensitive energetic compounds have been synthesized which consist of nitro and amino-substituted heterocycles. 4-Amino-3,5-dinitropyrazole (ADNP/LLM-116) is a dense, insensitive energetic compound with predicted performance approaching 85% of HMX, while 3-(4-nitro-1,2,5-oxadiazol-3-yl)-4-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-175) and 3-(5-amino-1,2,4-oxadiazol-3-yl)-4-nitro-1,2,5-oxadiazole (LLM-201) are attractive because of their melting temperatures of 100 °C and 101 °C, respectively. These compounds have been synthesized at the 20-40 gram scale and have been subjected to small-scale safety testing and their responses to impact, friction, and electrostatic discharge have been measured along with thermal stability testing. Chemical structures have been determined by spectroscopy and single crystal x-ray diffraction. Material detonation properties have been predicted relative to HMX and will be compared to experimental results. The equation of state of these compounds was determined by modeling the results from our newly developed small-scale rate stick, named the Disc-Acceleration Experiment (DAX). DAX uses less than 20 grams of sample material, and generates data for extracting detonation velocity, CJ-pressure and the detonation energy at volume expansions of ~3. The design is simple, and produces high-precision performance data that is comparable to traditional cylinder tests (CYLEX). The syntheses, material properties, relative performance and relative thermal stability of these new compounds are discussed.

Introduction

The goal of the energetic materials synthesis group at LLNL is to synthesize and scale-up energetic compounds in search of performance and safety that improves upon currently deployed materials. For any new material to find utility the cost must be controlled so our interests also lie in the improvement of the preparative routes of known materials. Our focus has been on the synthesis and characterization of unsaturated heterocycles with energetic nitro and desensitizing amino functional groups, such as LLM-105^[1]. By modulating the functional groups we seek to tune material properties such as melting point and thermal stability while increasing the density and improving on material sensitivities to mechanical insult.

A bottleneck exists in today's R&D environment where performance data is lacking on a large number of potentially useful new energetic materials. To address this, there exists a need for a high throughput, low cost performance test to allow for the evaluation of a large number of new materials with a modest amount (18-20 grams) needed for testing. Obtaining reliable data for detonation velocity, CJ pressure, and detonation expansion energy will allow for the direction of limited resources towards the further development of the most promising new materials.

The Disc Acceleration eXperiment (DAX), a small-scale rate stick with timing pins that includes a thin witness disc tracked by a PDV probe (Figure 1), has been developed at Lawrence Livermore National Laboratory and has been described recently.^[2] The current work details 3 insensitive energetic materials (Figure 2) that incorporate nitro and amino functional groups and their synthesis, properties, and results from Cheetah^[3] thermochemical equilibrium calculations along with DAX performance tests.

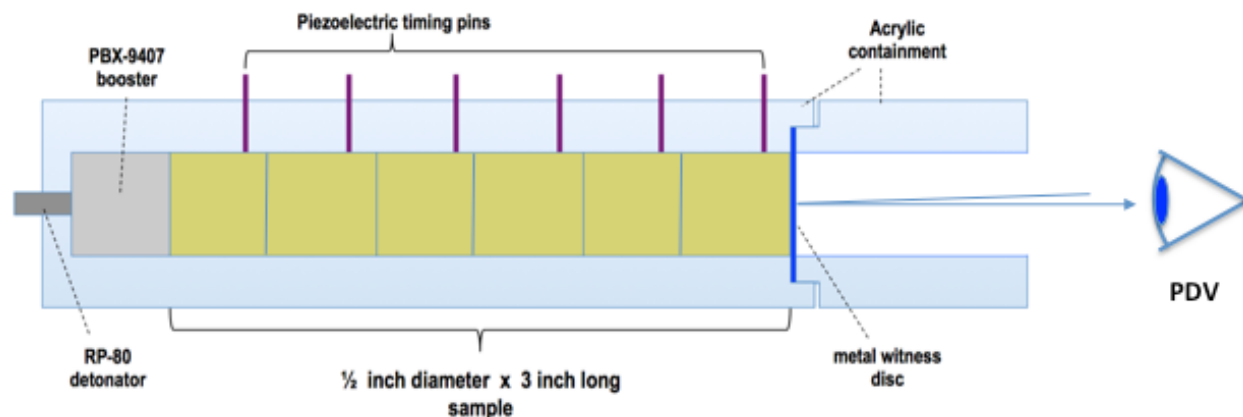


Figure 1: Schematic of the DAX test.

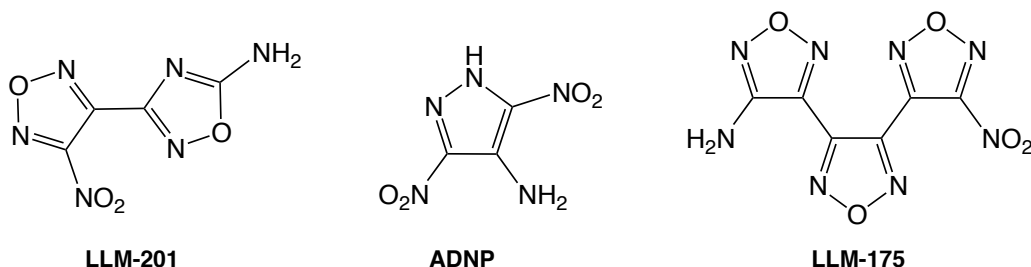


Figure 2: Insensitive energetic heterocycles featuring amino and nitro groups.

3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine (LLM-201):

The precursor to LLM-201, 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine, was reported in 2002^[4] in the *Russian Journal of Organic Chemistry*. Although the conversion of the amino groups to nitro groups was not mentioned for this particular compound, both the nitrosation and oxidative coupling of the amino furazan heterocycle was described. We initially were interested in condensing 2,2,2-trinitroethanol with the amino groups to prepare polynitroalkylamino oxadiazoles^[5] but were not able to observe any reactivity of the amine of the 5-amino-1,2,4-oxadiazole.

50g (0.3 mmol) of 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine was suspended in 100mL of trifluoroacetic acid and set to stir. 60mL (~1.8mol) of 80% hydrogen peroxide is added dropwise over one hour. The reaction mixture is stirred 24 hours at 30 °C. Filter through a glass fiber filter into 220g of crushed ice. The filtrate is stirred overnight, then filtered and set aside in a crystallization dish. The residue is washed with water and dried to yield 25g of crude LLM-201. The filtrate was allowed to evaporate, washed with water and dried affording an additional 10g of crude LLM-201. The material was crystallized from formic acid and water. MP: 100 °C; ¹H NMR (600 MHz) DMSO δ 7.51 (s, 2H); ¹³C NMR (150 MHz) DMSO δ 173.20, 159.23, 156.50, 140.79. A formulation of 5% estane and 95% LLM-201 was prepared and pressed into 6 0.5 inch diameter by 0.5 inch long pellets with an average density of 1.64 g/cc (96.7% TMD).

4-amino-3,5-dinitro-1*H*-pyrazole (ADNP/LLM-116):

4-amino-3,5-dinitro-1*H*-pyrazole^[6] first appeared in the literature in 1993^[6]. A footnote to a synthetic approach is mentioned^[7] in 1997 and combustion calorimetry studies^[8] were presented in 1998. The first described synthesis was in 2001^[9] from 3,5-dinitropyrazole and 1,1,1-trimethylhydrazinium iodide. The room temperature crystal density was reported to be 1.900 g/cc. For this work we employed the recent synthesis from Daling^[10] from 4-chloro-3,5-dinitropyrazole and ammonium hydroxide at high pressure for our experiments. 20 gram batches of ADNP were prepared using a 0.5L glass pressure vessel with a Teflon screw-cap and EPDM gasket. A hand-mixed formulation of 5% polyisobutylene and 95% ADNP was prepared and pressed into 6 0.5 inch diameter by 0.5 inch long pellets with an average density of 1.722 g/cc (95.4% TMD).

3-(4-nitro-1,2,5-oxadiazol-3-yl)-4-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-175):

LLM-175^[11] has been synthesized by reduction of 3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole *N*-oxide^[12] with triethylphosphite followed by oxidation with 30-70% hydrogen peroxide in sulfuric acid. This method yields a mixture of LLM-175 and 3,4-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (LLM-172), with the ratio dependent on the concentration of hydrogen peroxide used. To maximize the percent of LLM-175, a 5L flask is charged with 750mL conc. sulfuric acid to which 50g (0.21mol) 3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole was added and cooled to 10-15 °C. 150 mL (~1.7 mol) 35% hydrogen peroxide is added dropwise, keeping the temperature between 15-25 °C. Let the reaction stir for 4-5 hours, at which point the LLM-172 precipitates from the reaction mixture and is filtered through a glass fiber filter into 2.5kg ice water. Collect the precipitated LLM-175 by suction filtration, wash with water and dry in air to yield 25 grams of LLM-175 as a white solid. Further purification is achieved by sublimation or recrystallization. MP: 100 °C; ¹H NMR (600 MHz) DMSO δ 6.72 (s, 2H); ¹³C NMR (150 MHz) DMSO δ 160.66, 156.02, 144.85, 141.52, 139.83, 136.29. A hand-mixed formulation of 5% polyisobutylene and 95% LLM-175 was prepared and pressed into 6 0.5 inch diameter by 0.5 inch long pellets with an average density of 1.635 g/cc (96.0% TMD).

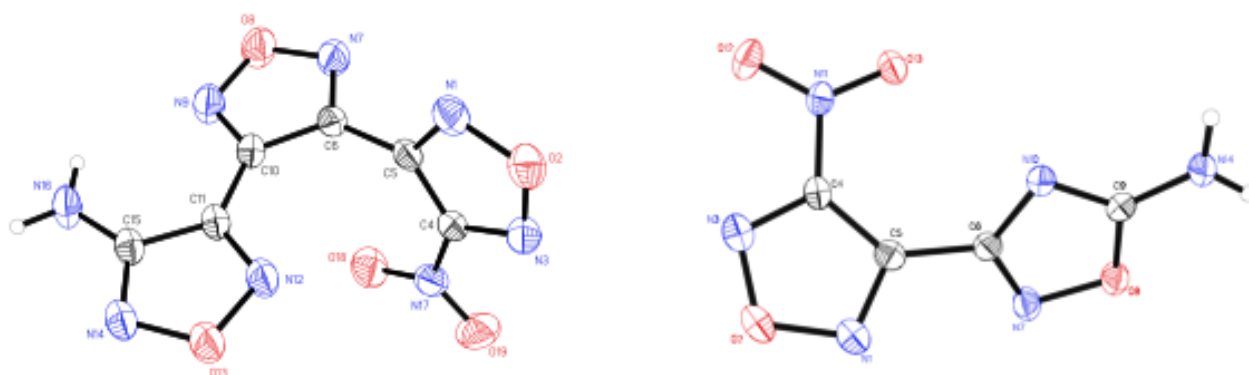


Figure 3: X-ray crystal structures of LLM-175 (left) and LLM-201 (right). Thermal ellipsoids are drawn at the 50% level.

Results and Discussion

To assess the handling hazards of new energetic materials the response of a small amount of the material to impact, friction, and spark is measured. While these small-scale safety tests are flawed, the results of these tests along with information from a DSC and the LLNL Chemical Reactivity Test, or CRT (similar to vacuum thermal stability testing), allow

comparison to other well characterized explosives. The results of these tests are shown in table 1. None of the materials showed any response to a spark of 1J with 510ohm resistance, which simulates the static discharge from the human body^[13]. The data for TATB and HMX are included for comparison. All three explosives are less sensitive to impact and friction than HMX. LLM-201 has good thermal stability as shown by a high DSC exotherm onset temperature. The CRT test results in the generation of 0.1cc of gas per gram of LLM-201 after 22 hours at 80 °C, which corresponds to roughly 0.02% mass loss. The force required to elicit a response from impact and friction exceeded the limits of our testing apparatus, similarly to TATB. This leads us to conclude that LLM-201 is a reasonably insensitive material.

Table 1: Small-scale safety test and thermal testing results

Sample	Dh ₅₀ ^[14] cm	BAM Friction (# go @ kg)	DSC onset °C	CRT cc/g @ °C
LLM-201	>177	0/10 @ 36	261	0.1 @80
ADNP	168	0/10 @ 36	179	0.6 @80
LLM-175	>177	1/10 @ 24	234	0.9 @120
TATB	>177	0/10 @ 36	381	0.1 @120
HMX	32	1/10 @ 16	279	0.1 @120

The response to impact of LLM-175 is beyond the limits of our test, while ADNP showed reactions of 50% probability from a drop height of 168cm. This corresponds to approximately 41J of energy transferred using our 2.5kg drop weight. For comparison, HMX has a 50% probability of response from about 8J of energy. Interestingly, ADNP does not respond to 36N of friction while LLM-175 reacts 1/10 times with 24N of friction force. LLM-175 has good thermal stability, less than 0.2% mass loss after 22 hours at 120°C, an onset of decomposition greater than 230 °C and melts at 100 °C. ADNP has a lower decomposition temperature and decreased thermal stability compared to the other materials tested.

Table 2: Inputs used for Cheetah 7.0 calculations

Sample	Molecular formula	ΔH_f (kcal/mol) ^[15]	Crystal density @ 293K
LLM-201	C ₆ H ₂ N ₆ O ₄	+46.3	1.736
ADNP	C ₃ H ₃ N ₅ O ₄	-0.2 ^[8]	1.900
LLM-175	C ₆ H ₃ N ₈ O ₅	+159.5	1.782

To estimate the performance of explosives using the Cheetah code the molecular formula, density, and heat of formation are needed. These properties are listed in Table 2. The results from Cheetah for the pure materials and the tested formulations are listed in Table 3. The velocity of detonation, the CJ pressure, the total energy at V_{2.2}/V₀, and the energy relative to the HMX formulation at 2.2 volume expansions are given. Not surprisingly, ADNP has the highest predicted detonation velocity and CJ pressure, followed by LLM-175, and LLM-201. Interestingly, LLM-175 is predicted to be the most energetic at 2.2 volume expansions.

The results for the metal witness discs of DAX tests from LLM-201, ADNP, and LLM-175 are presented in Figure 4 as the velocities of the discs versus time. Also shown are the results from JWL model simulations for the formulations. The detonation velocities are taken from the piezoelectric timing pins (not shown).

Table 3: Cheetah 7.0 results

Formulation	%TMD	VD (km/s)	CJ (GPa)	E ₃ kJ/cc	E ₃ Norm
Neat LLM-201	100	7.80	24.5	5.75	0.81
LLM-201 w/ 5% estane	96.7	7.52	22.1	4.87	0.69
Neat ADNP	100	8.68	32.8	6.85	0.97
ADNP w/ 5% PIB	95.6	7.74	23.5	5.48	0.78
Neat LLM-175	100	8.10	27.0	6.94	0.98
LLM-175 w/ 5% PIB	97.0	7.41	25.1	5.78	0.82
HMX	100	9.25	37.19	8.66	1.23
HMX w/ 5% PIB	96.0	8.37	29.5	7.06	1.00
TATB	100	8.45	30.2	6.19	0.88
TATB w/ 5% PIB	96.0	7.50	21.2	4.98	0.71

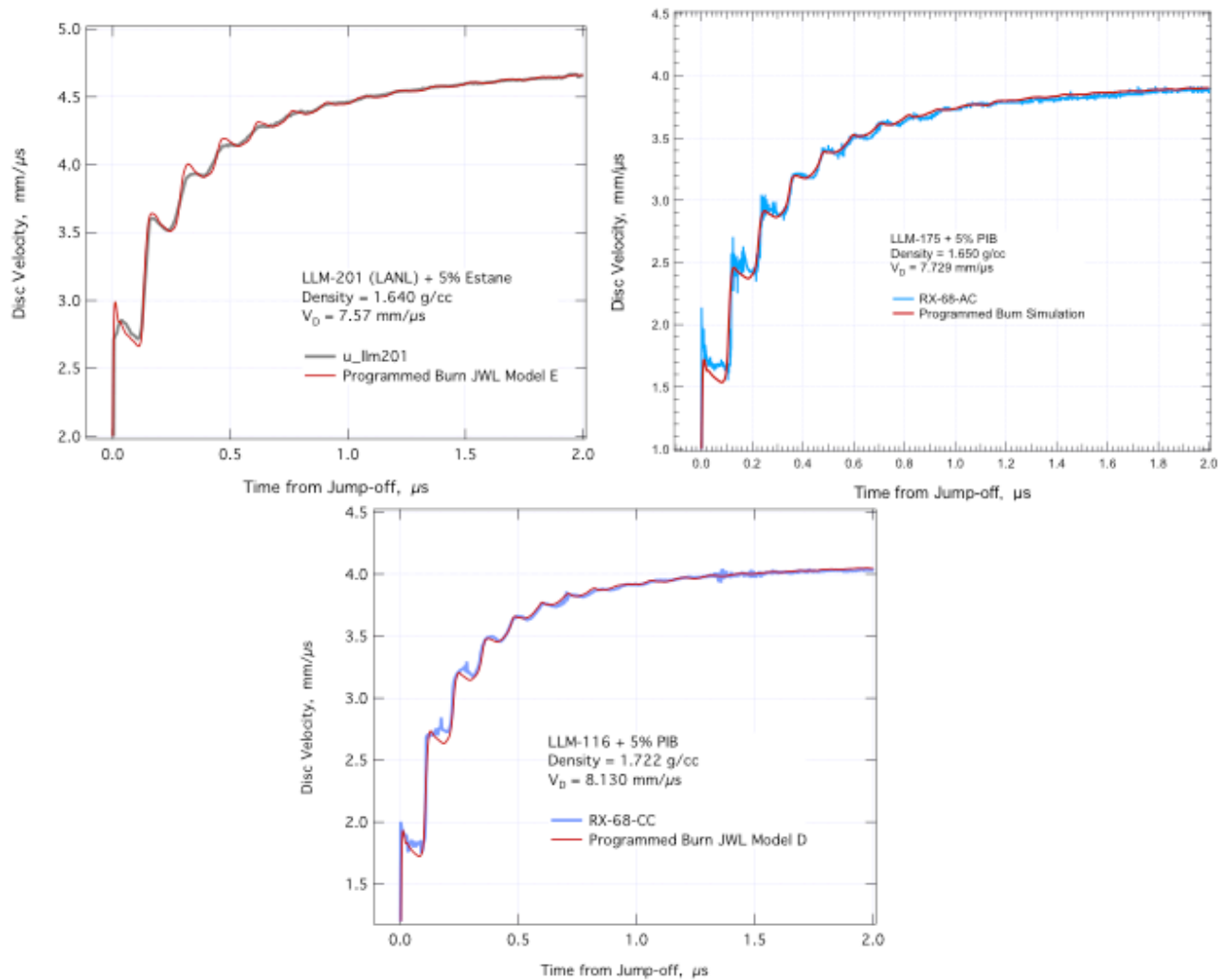
**Figure 4:** DAX disc velocities vs. time traces for LLM-201 (left), ADNP/LLM-116 (center), and LLM-175 (right) along with JWL programmed burn simulations.

Table 4: Explosive performance of LLM-201, ADNP, and LLM-175 formulations.

Sample	Density/%TMD	VOD (km/s)	CJ Jump-off	JWL CJ	DAX E ₃ kJ/cc
LLM-201 95%	1.64/96.7	7.757	23.8	23.8	4.46
ADNP 95%	1.722/95.4	8.130	28.9	28.9	4.84
LLM-175 95%	1.650/96.0	7.729	31.4	24.5	5.01

Table 4 summarizes the results from the DAX experiments and for the JWL modeling for the three explosive formulations. The CJ pressure is extracted from the velocity time records near the jump-off region, and has been described in detail.^[2] The data is in good agreement with the experiments for LLM-201 and ADNP. The measured detonation velocities are all higher than the Cheetah values from Table 3 and the CJ pressures are in good agreement except in the case of the LLM-175 formulation. The LLM-175 formulation also displays the highest energy at 3 volume expansions. This may be due in part to the slightly higher density of the LLM-175 pressings, compared to ADNP.

Conclusions:

The synthesis and properties of three moderately insensitive explosives has been presented. Explosive performance of three formulations has been calculated using Cheetah and measured using the DAX test. The results from DAX can be used for the modeling of the equation of state for new explosives, with less than 20 grams of material. This technique should prove useful for directing research efforts towards the further development of the most promising new materials.

Acknowledgements:

We are grateful to Elizabeth Francois from Los Alamos National Laboratory for the formulation, pressing, and DAX experimental results on LLM-201. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-CONF-XXXXXX. We are grateful for funding of this work from the Joint DoD / DOE Munitions Technology Development Program (JMP) and from LDRD 12-ERD-066.

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